A Chemist's View of Inelastic Neutron Scattering

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Advantages of INS in molecular spectroscopy:

Absence of selection rules

Sensitivity to isotopic substitution, especially D for H

Ease of calculation of spectral intensities

Disadvantages relative to IR and Raman:

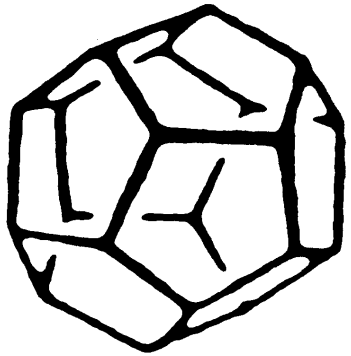
Relatively large samples and long experiment times

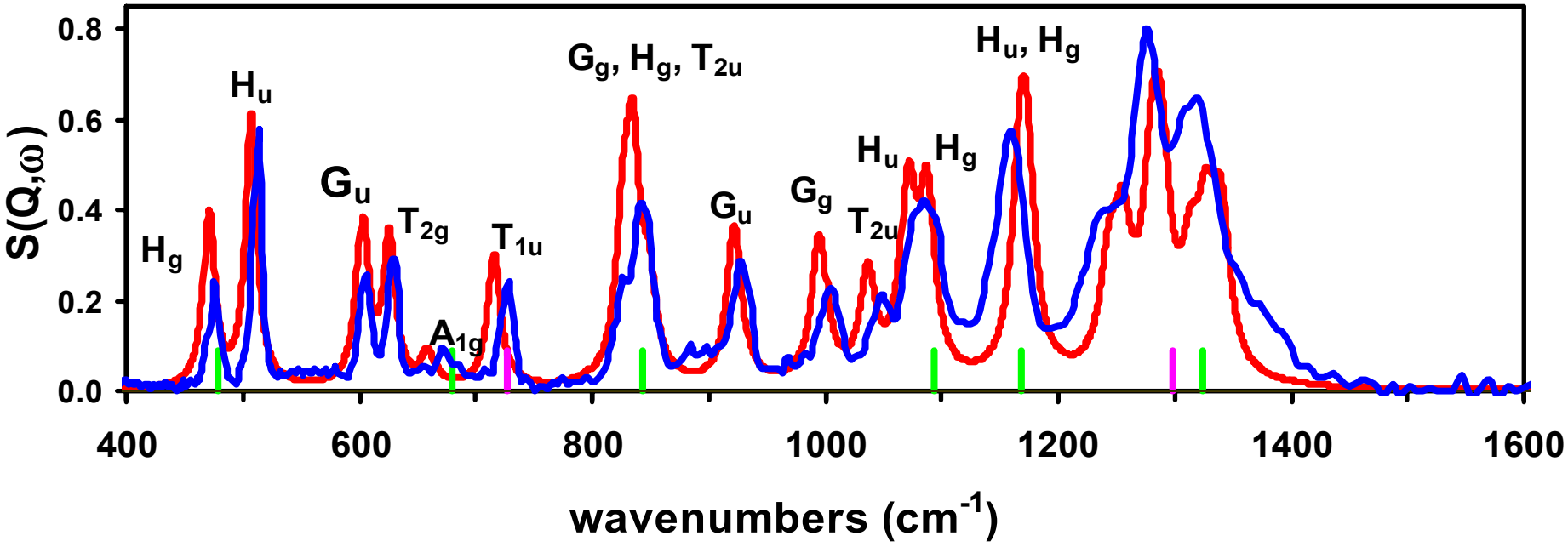
Lower resolution

Topics to be covered

- Dodecahedrane: a high-symmetry alkane
- Hydrogen bonded systems illustrating:
  - Short, strong low-barrier or zero-barrier (centered) hydrogen bonds;
  - Cooperative hydrogen bonding;
  - Multiplicity of H-bonding motifs relevant to crystal engineering, polymorphism and protein structure.

Dodecahedrane, $C_{20}H_{20}$

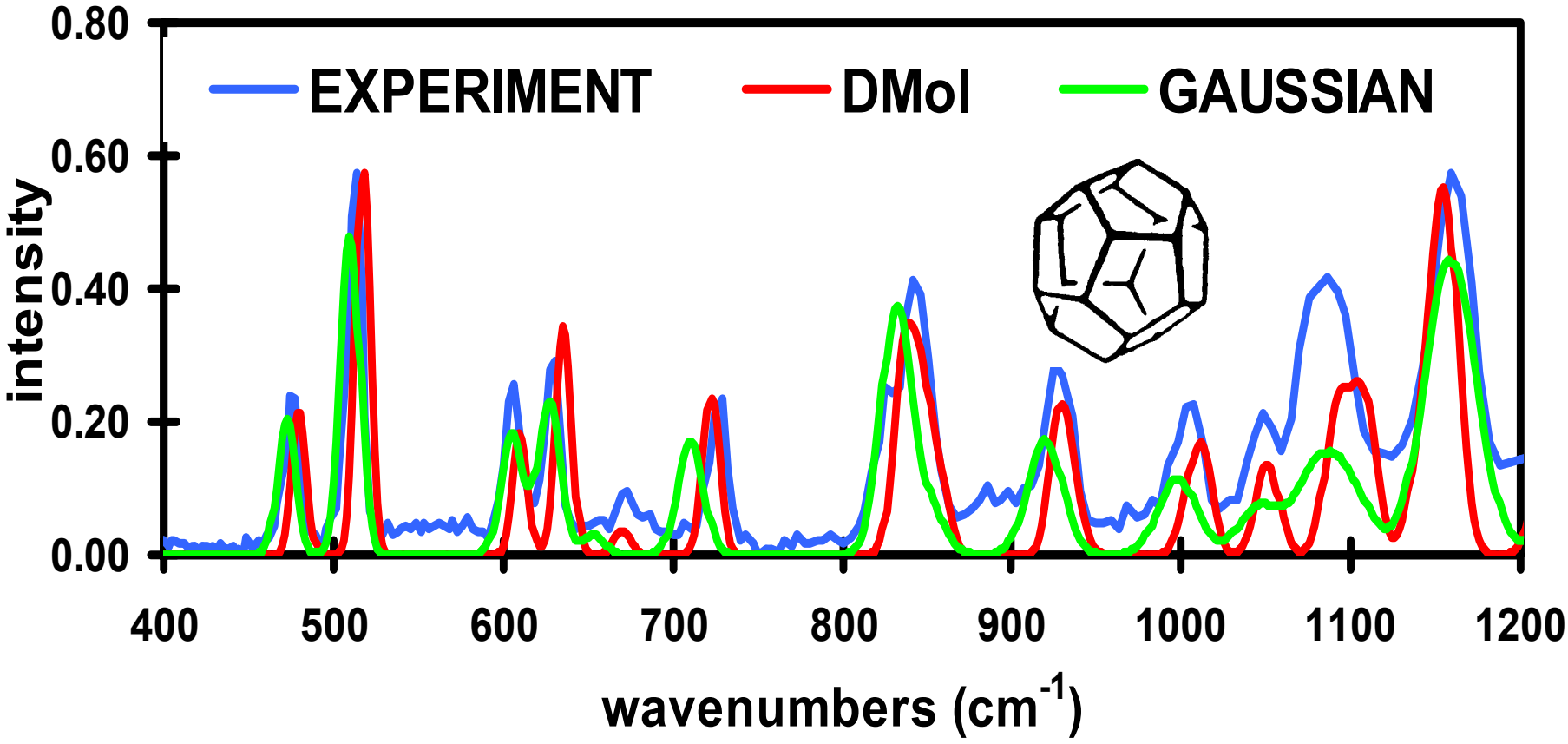




I_h symmetry. 30 distinct vibrations. IR: $3T_{1u}$; Raman: $2A_g + 6H_g$

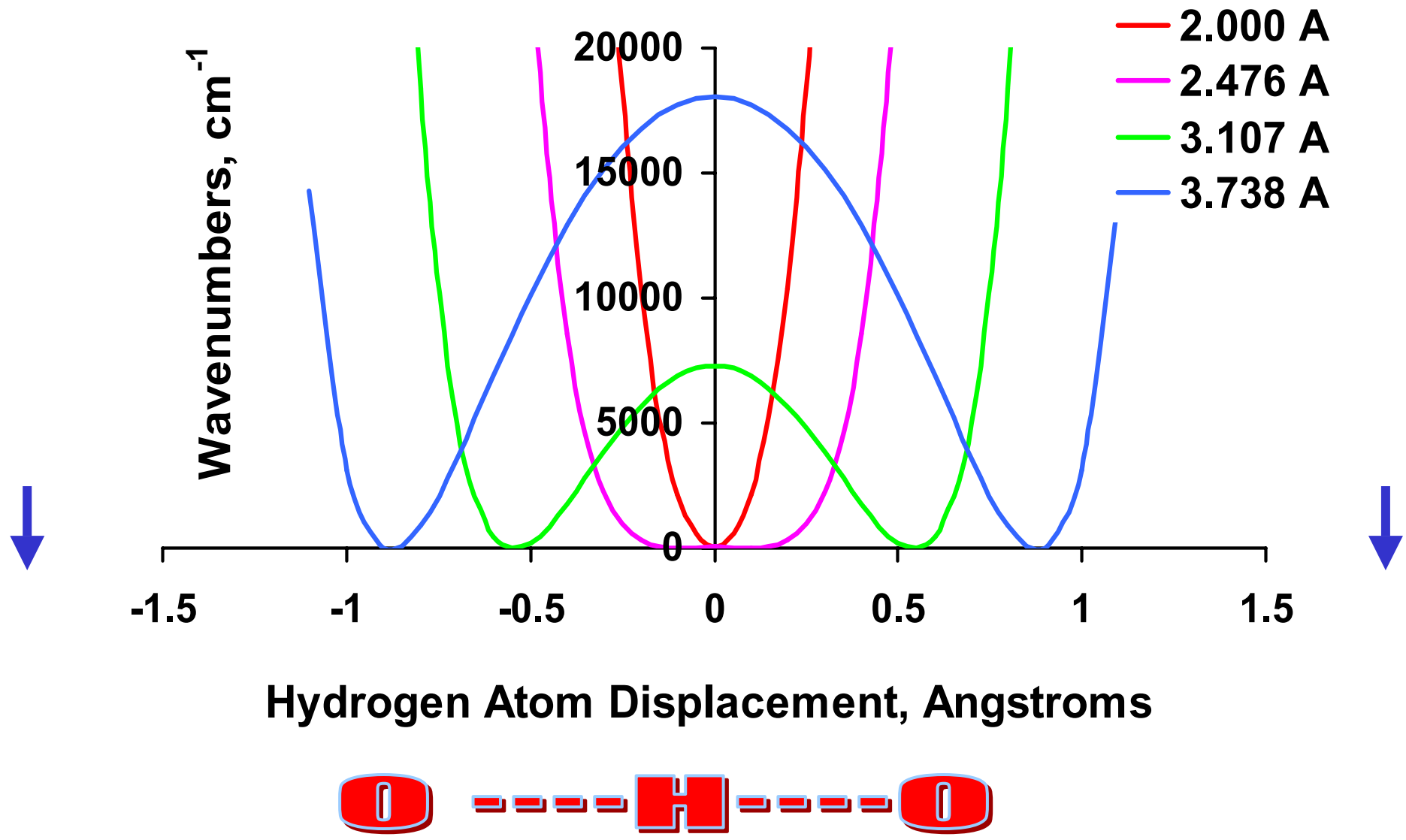
$2A_g+1T_{1g}+2T_{2g}+4G_g+6H_g+3T_{1u}+4T_{2u}+4G_u+4H_u$

Dodecahedrane INS: Experiment, Gaussian and DMol3 Periodic DFT Calculations

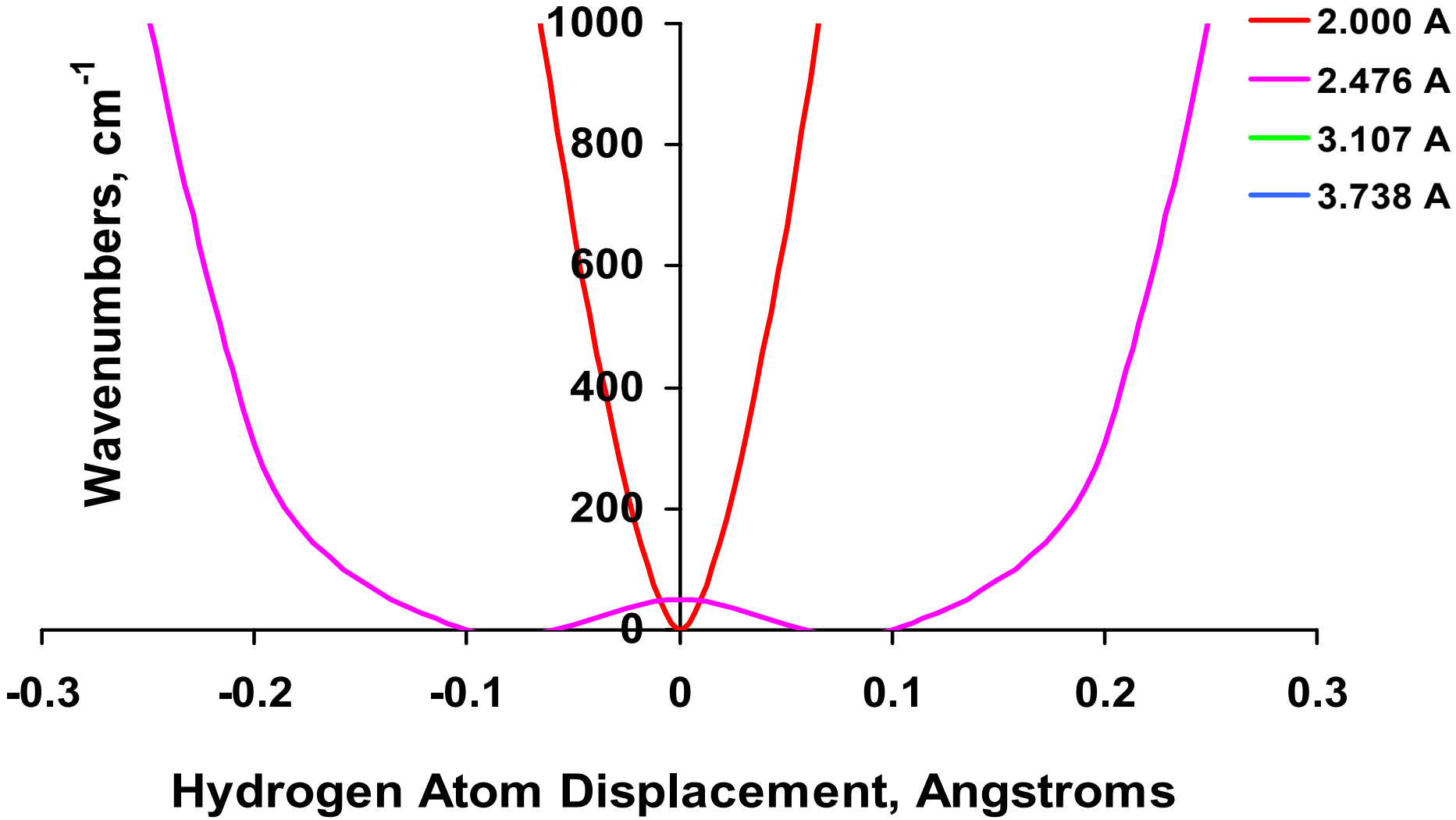


Short, strong, low-barrier hydrogen bonds

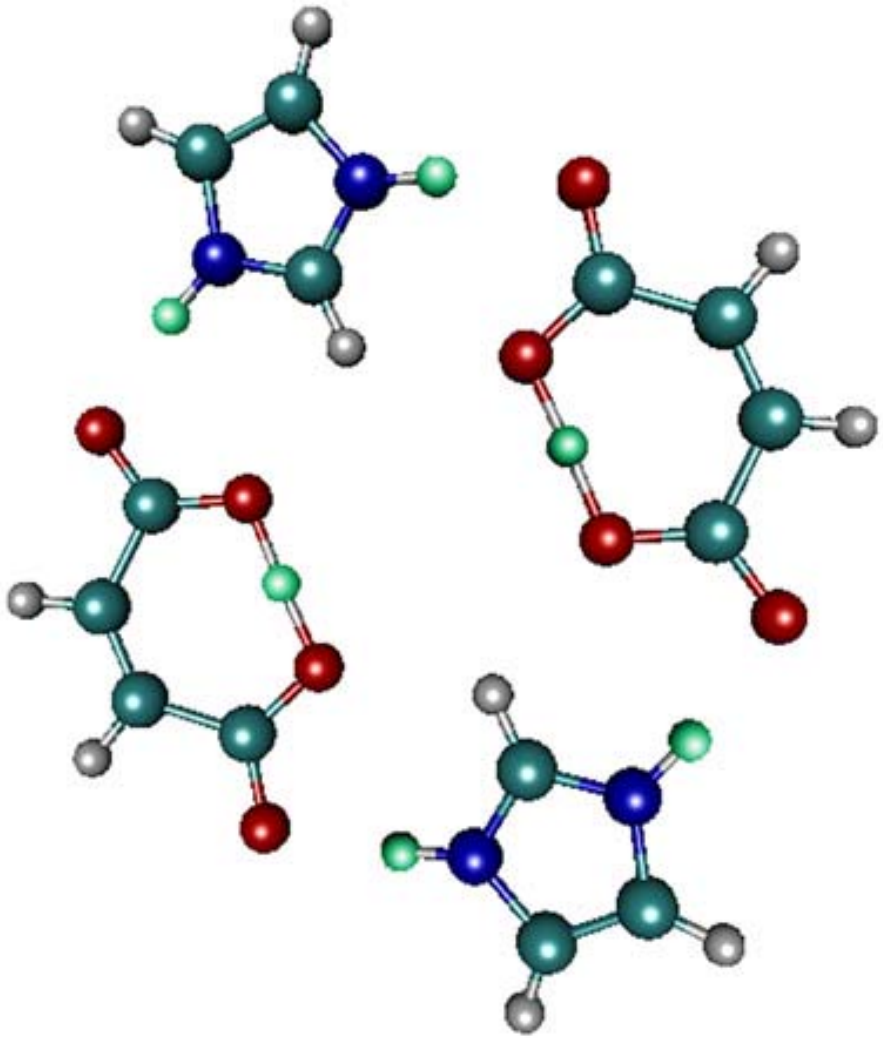
- Speakman-Hazdi compounds
- For O-H•••O hydrogen bonds, R_{oo} < 2.6 A
- The shortest distances are observed for anionic oxygen complexes in which case the proton transfer potential becomes symmetric: [O-H•••O^- ↔ O^- •••H-O].
- For large R_{oo} the energy for this process is the O-H bond strength.


2.000 A
2.476 A
3.107 A
3.738 A
Wavenumbers, cm-1
20000
15000
10000
5000
0
-1.5
-1
-0.5
0
0.5
1
1.5
Hydrogen Atom Displacement, Angstroms
O ----H----O

Expanded view of the potentials for the two shortest O-O distances considered



imidazolium hydrogen maleate

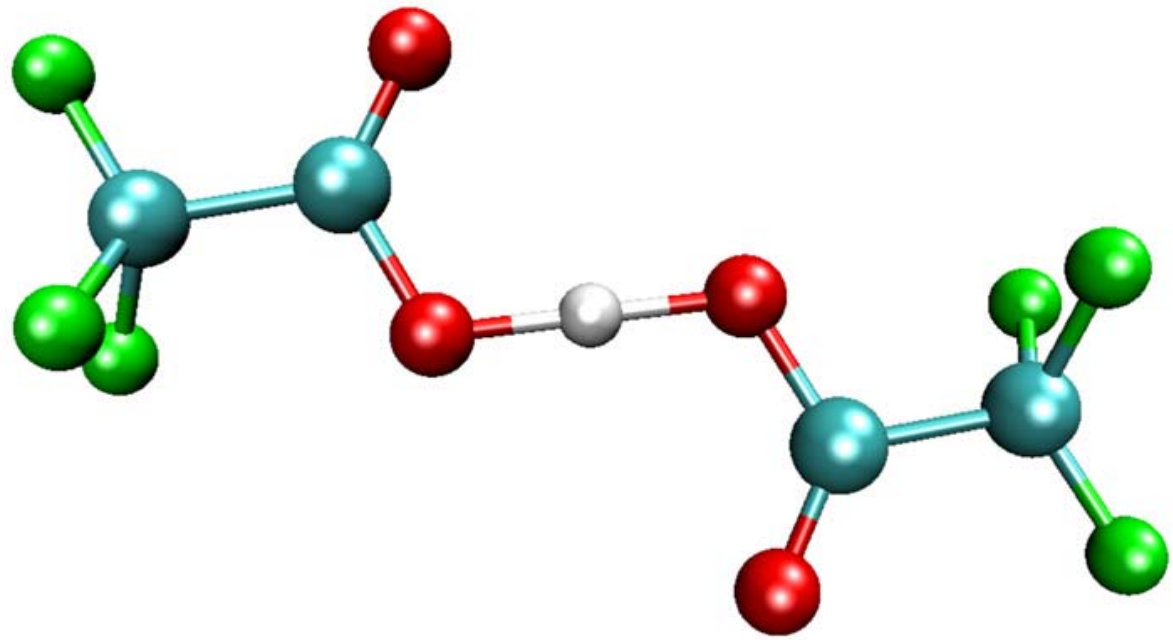


O-O distance = 2.393(3) A

James & Matsushima, Acta Cryst B32, 1708 (1976); Hsu & Schlemper, Acta Cryst. B36, 3017 (1980)

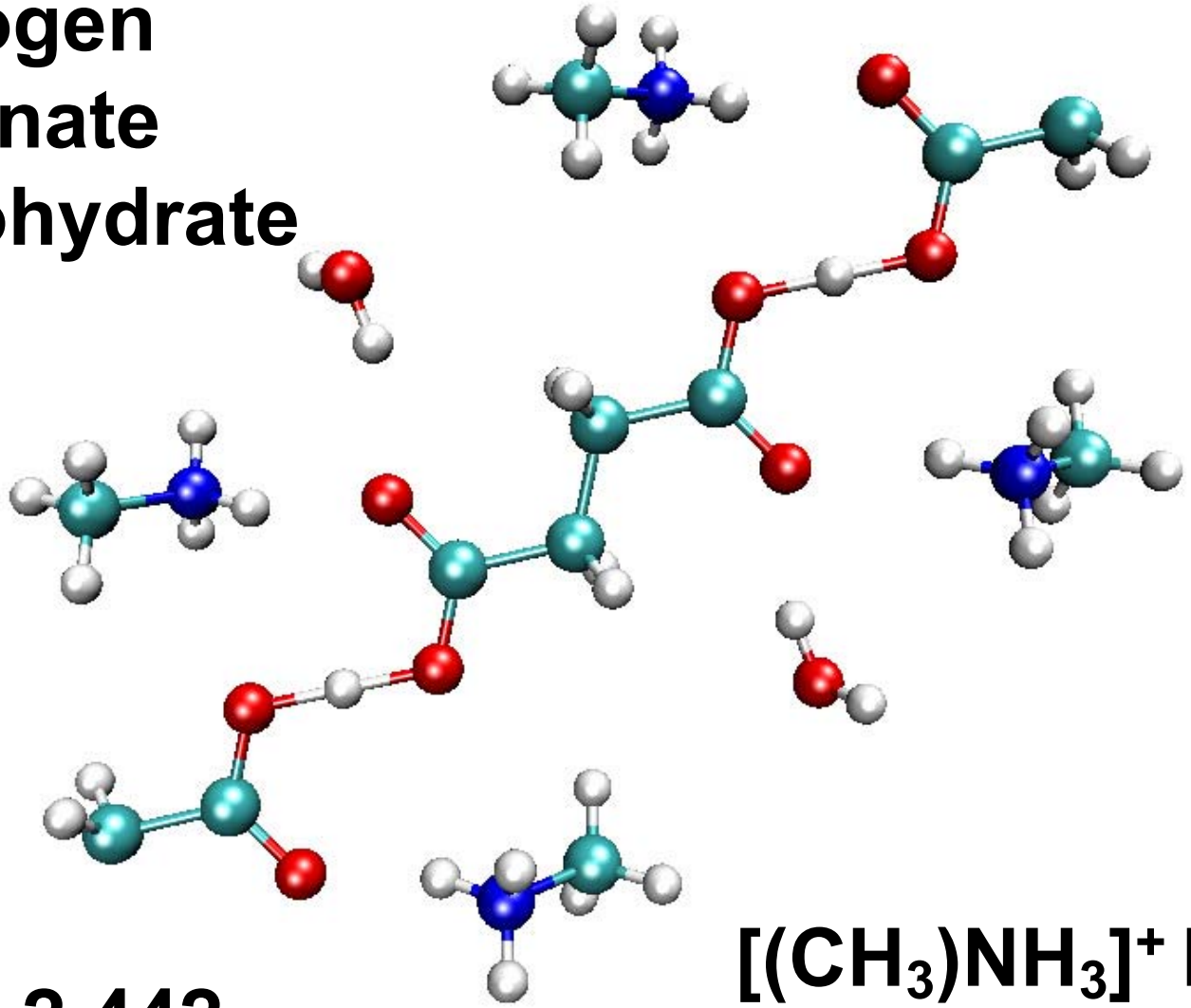
Potassium Hydrogen Bistrifluoroacetate

Hydrogen bond O-O distance: 2.437 Å



Macdonald, A. L.; Speakman, J. C, and Hadzi, D., J. Chem. Soc. Perkin II, 825 (1972)

methylammonium hydrogen succinate monohydrate

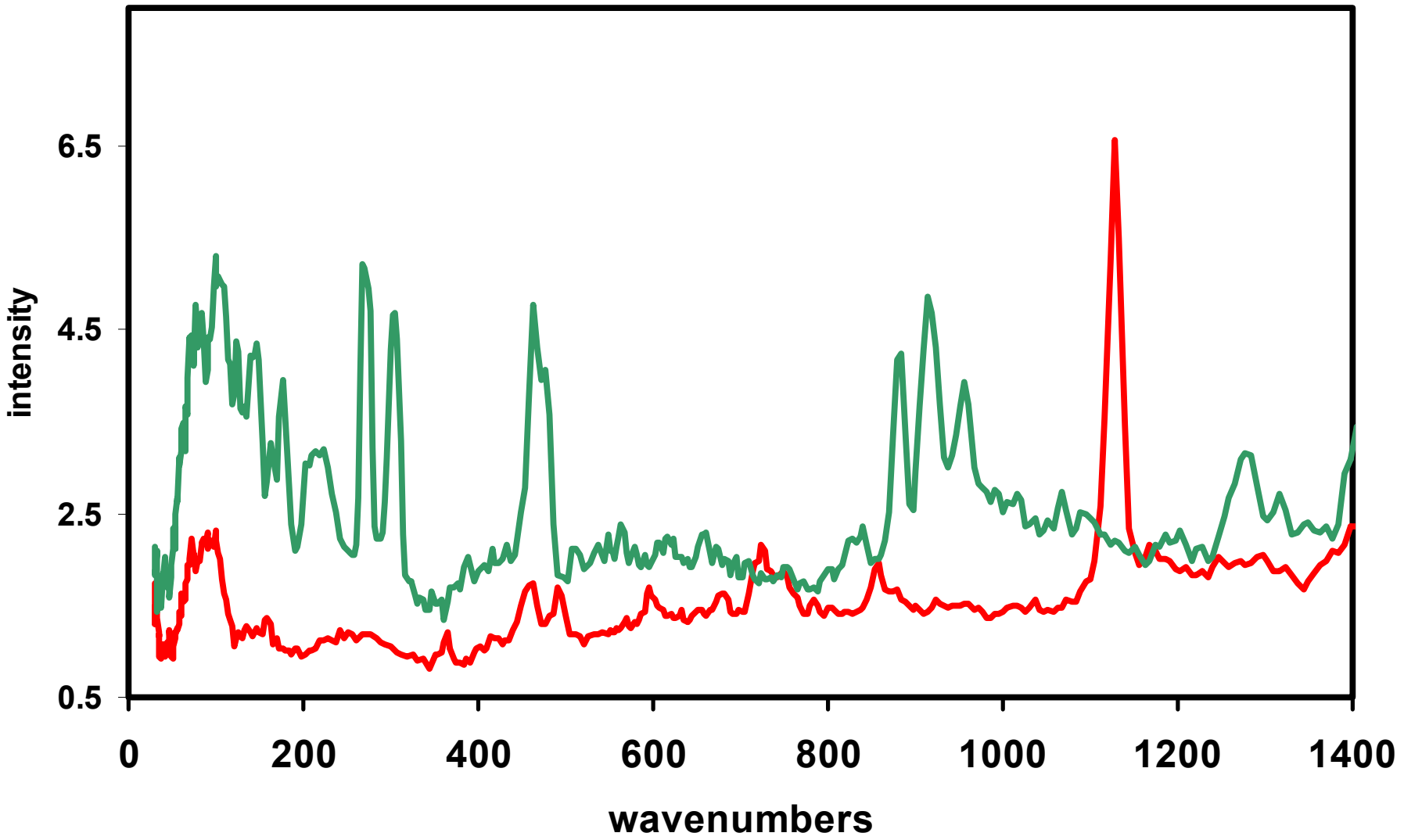


$R_{OO} = 2.442$

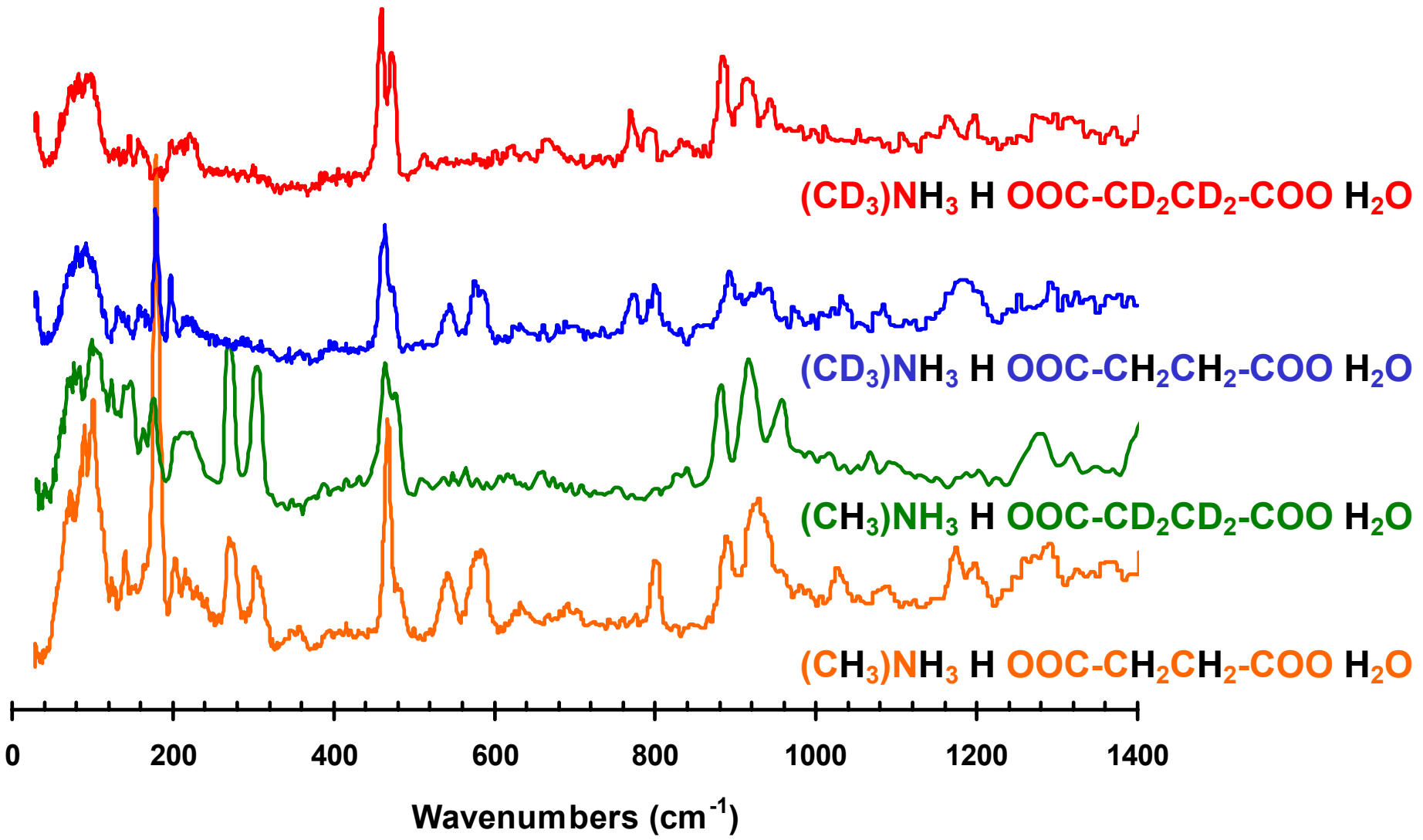
$[(CH_3)NH_3]^+ H^+ {}^-OOCCH_2CH_2COO^- H_2O$

KH oxalate O-O = 2.514 (red line)

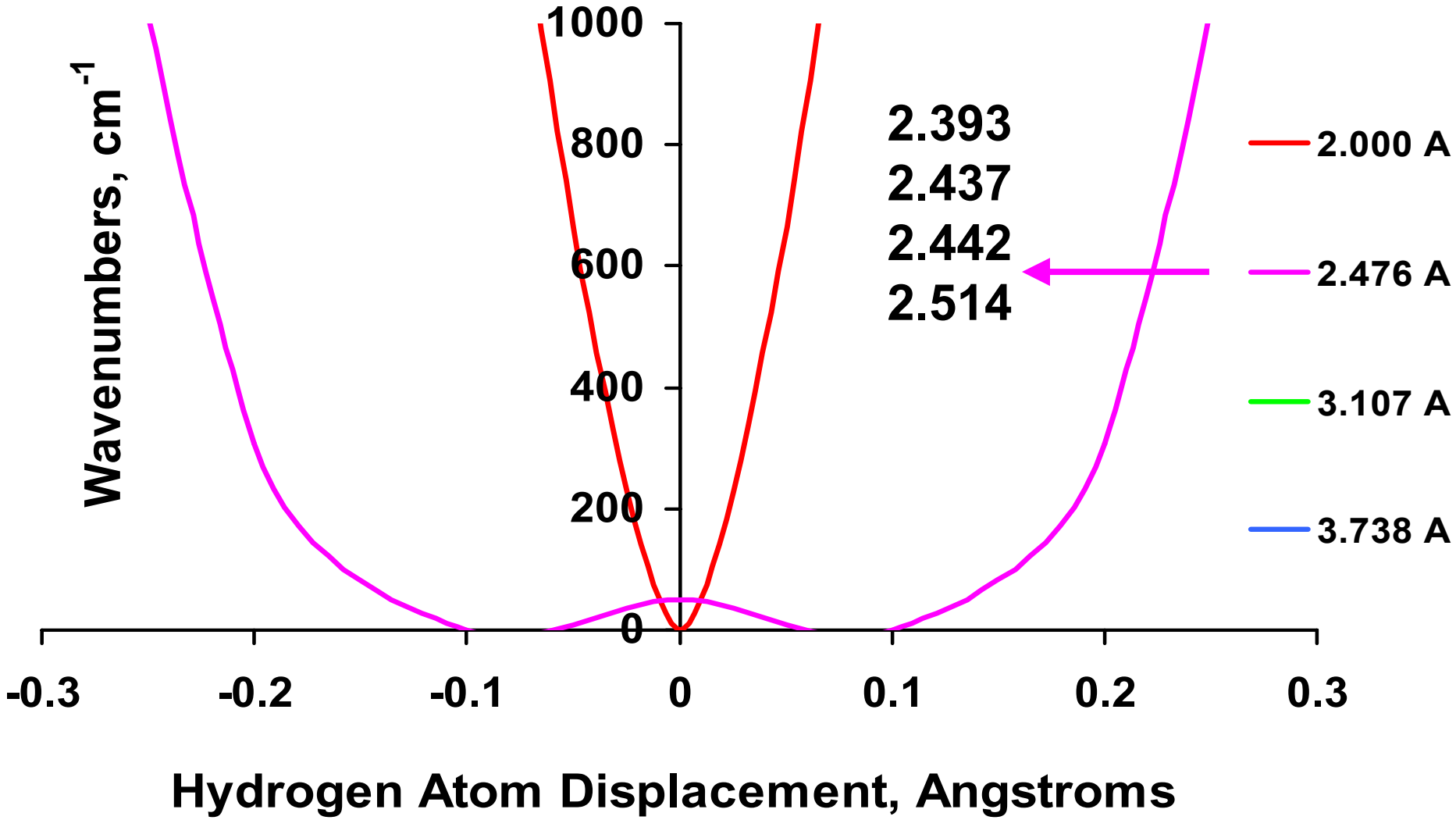
$(CH_3)NH_3$ H succinate-d_4 H2O O-O = 2.442 (green line)



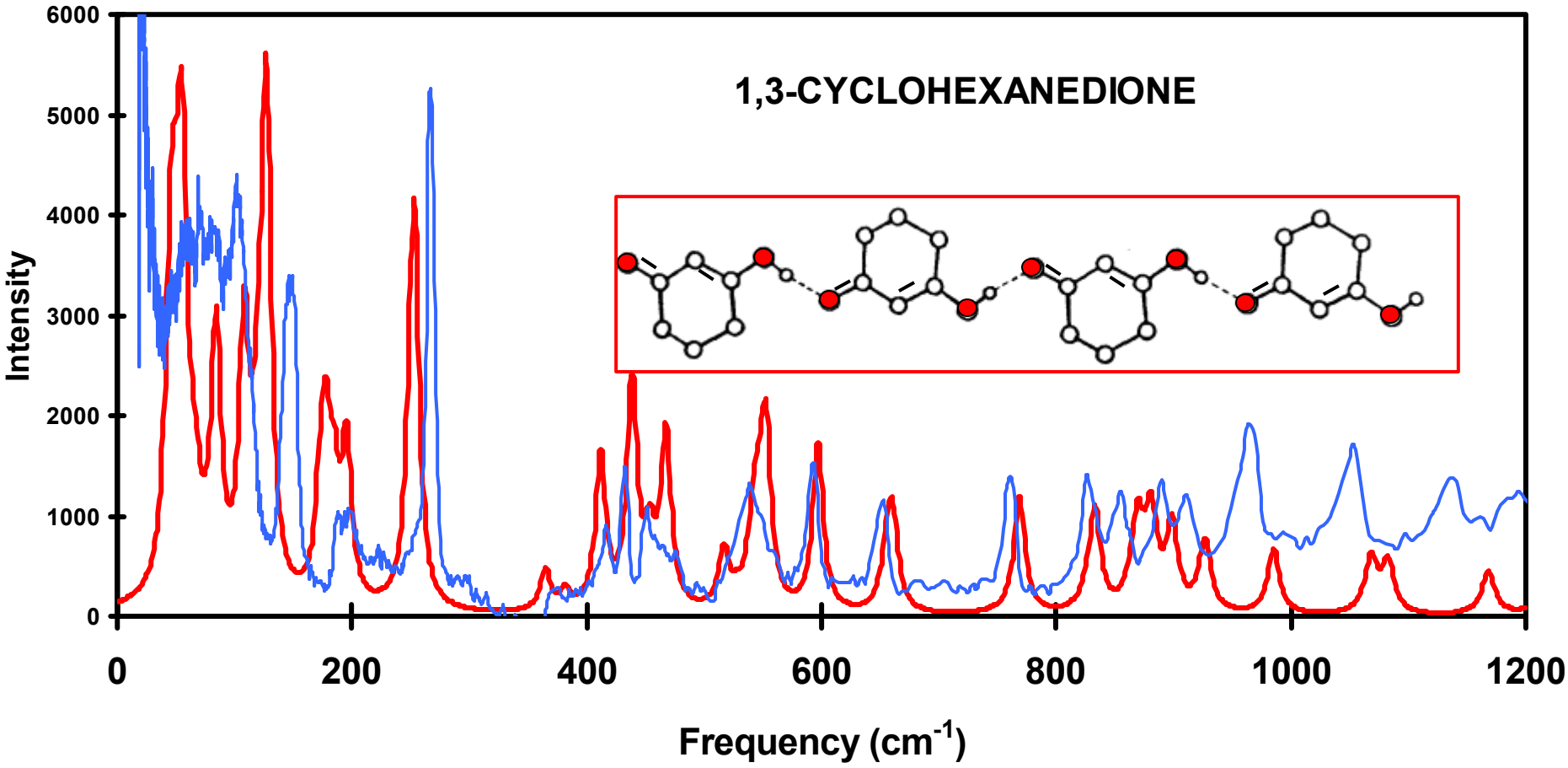
INS spectra of selectively deuterated methylammonium hydrogen succinate monohydrate



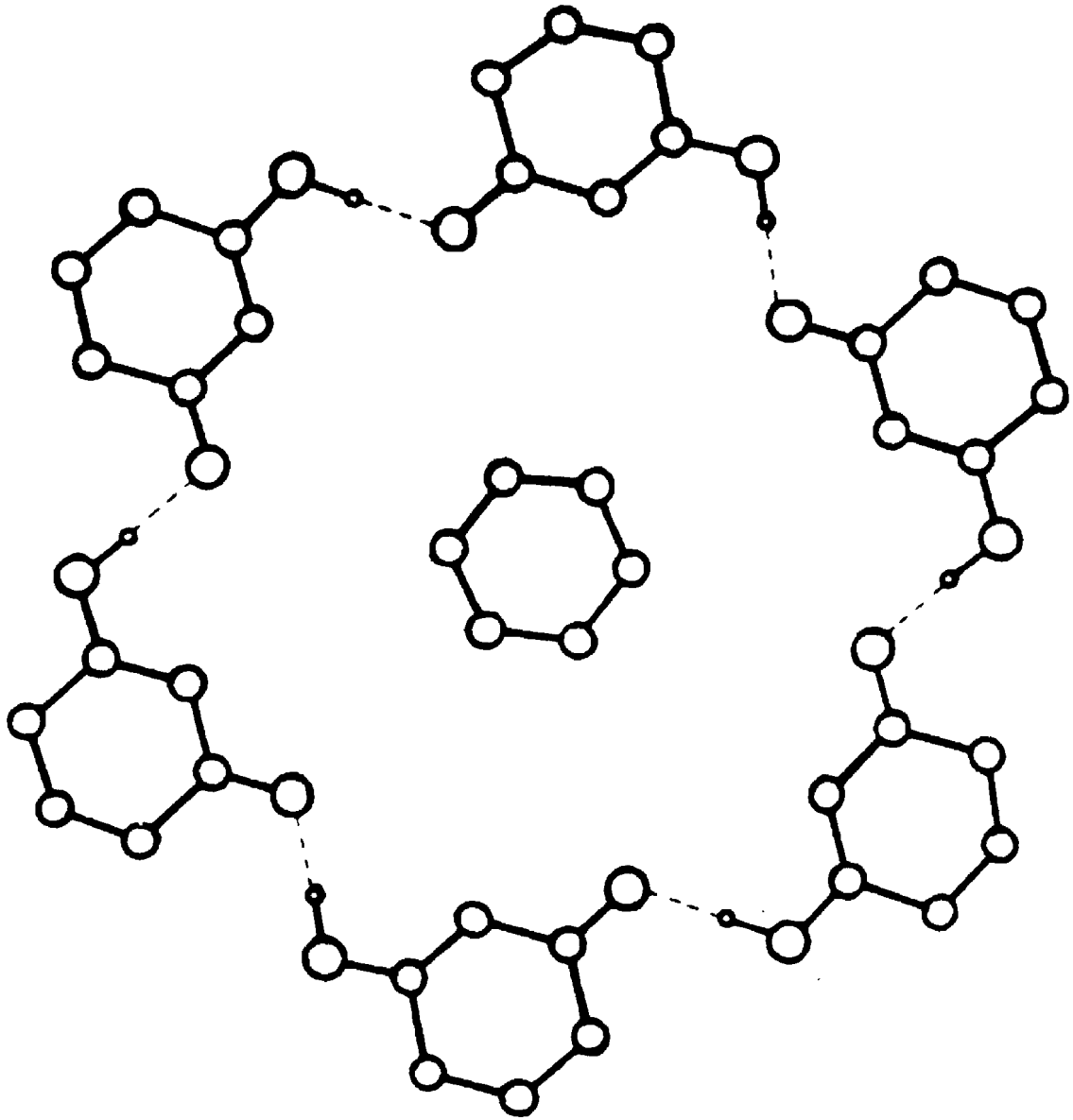
Comparison of calculated potentials and actual cases considered

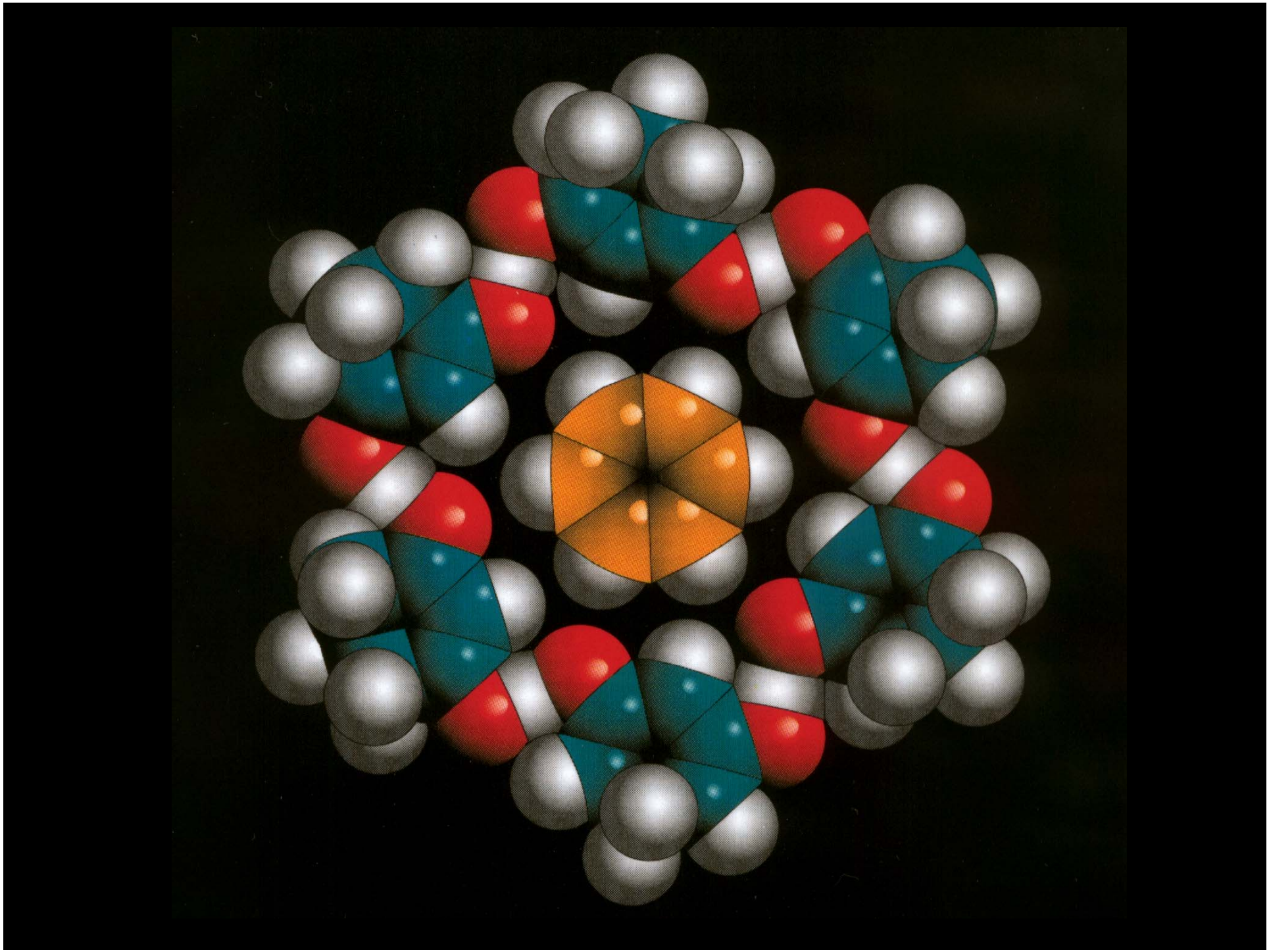


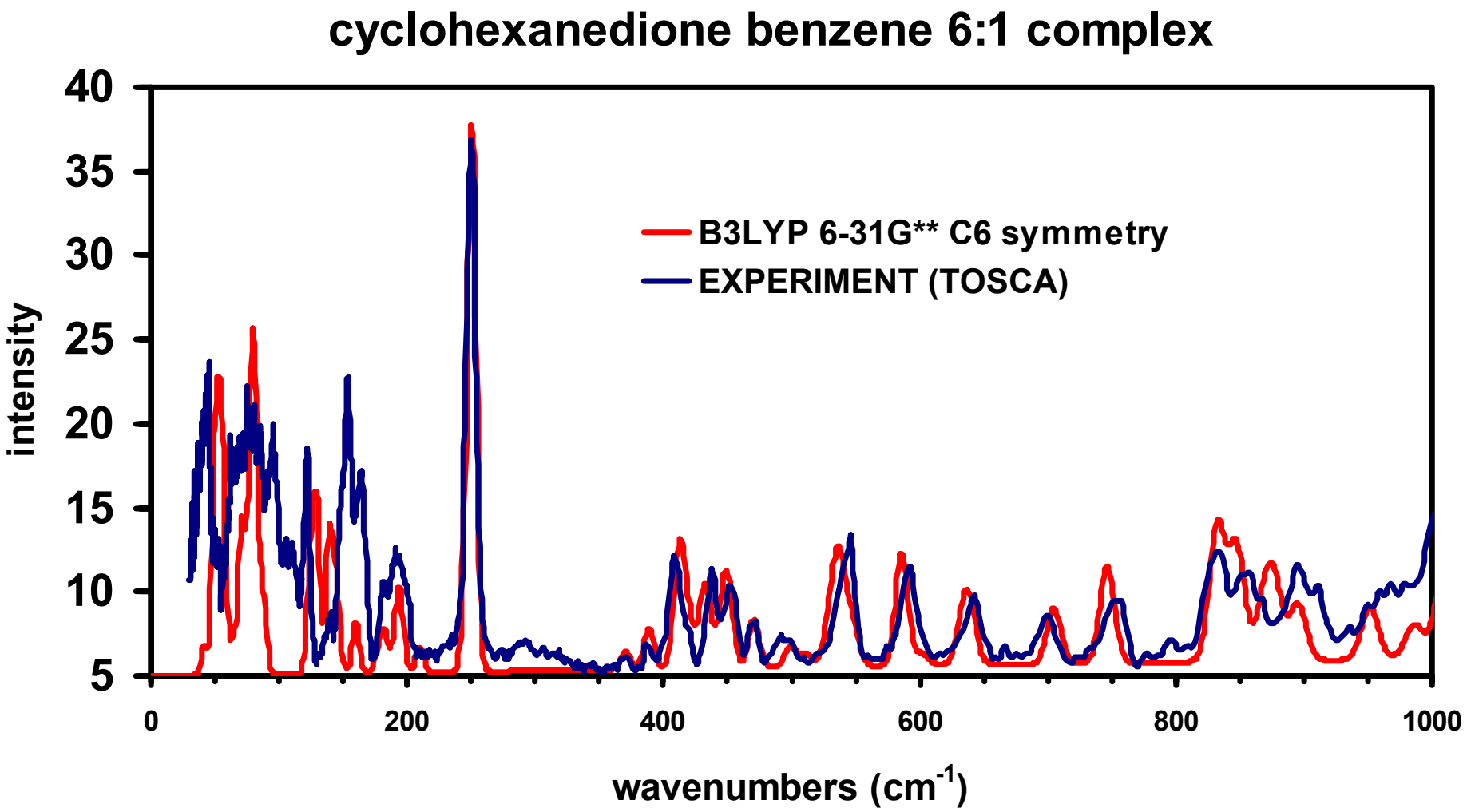
Cooperativity in H-bonded motion



$R_{OO} = 2.56$







The self-contained nature of this complex means that it can be adequately treated as a single “super-molecule”. The results indicate that DFT methods are adequate for standard H-bonds.

The Big Picture: Crystal Engineering, Polymorphism and Protein Structure

- Crystal engineering is aimed at making interesting and perhaps useful NLO and charge transfer materials, organic magnets, etc. But organic molecular crystal structures cannot be predicted.
- Polymorphism indicates that crystal structures are not unique and is a big problem for the pharmaceutical industry.
- The pattern of hydrogen bonding determines the structure of proteins – and thus their function as enzymes and structural elements.

A few points to consider

- A model of a molecular crystal that provides an accurate description of the vibrations must contain an accurate description of the structure, more accurate than that determined by x-ray diffraction data in most cases.
- The most stable form of a molecular crystal is the one with the lowest free energy. The vibrational contributions to the entropy may be very important at finite temperature.
- The crystals that form may be the ones that form most quickly and may not be the most stable form.

Summary of approach

- **INS provides a structure-sensitive picture of molecular vibrations in a crystal.**
- **Theory that describes these vibrations, describes the structure with high precision.**
- **Short H-bonds provide a severe test of theory.**
- **The resulting structures can be compared to other alternative structures at the free energy level.**